FR 1,071,945

Job No.: 1505-88752
Translated from French by the Ralph McElroy Translation Company
910 West Avenue, Austin, Texas 78701 USA

FRENCH REPUBLIC
MINISTRY OF INDUSTRY AND COMMERCE
DEPARTMENT OF INDUSTIAL PROPERTY
FRENCH PATENT NO. 1,071,945

Gr. 1. - Cl. 4.

Filing Date:	December 19, 1952, 3:07 p.m., in Paris
Date Granted:	March 10, 1954
Date Published:	September 7, 1954
Priority:	Patent application filed in Switzerland December 21, 1951, in the name of the applicant

PROCESS FOR PROTECTION OF WORKED MATERIALS FROM ATTACK BY LOWER FUNGI AND MATERIALS TREATED USING THIS PROCESS

Applicant:	Company known as: CIBA (Joint-Stock company) residing in Switzerland

It is known that salicylanilide can be used for protection of textiles, leather and other materials and also of the higher plants from attack by the lower fungi.

The present invention relates to a process for the protection of worked materials which are susceptible to attack by the lower fungi, characterized by the fact that these materials are treated by salicylanilides, which are halogenated in the aniline nucleus. The process according to the invention is particularly suitable for the protection of materials containing cellulose from attack by the lower fungi which degrade cellulose, since the anilides halogenated in the aniline nucleus are more active than ordinary anilide with regard to molds which degrade cellulose, when the lower fungi only have available, as culture ground, an agar jelly containing inorganic salts and a cellulose-containing material as carbon source, that is to say when the lower fungi must live under conditions such that they degrade cellulose and destroy cellulose-containing material.

Considered among the monohalogenated derivatives which can be used according to the invention are the various monochloro-, monobromo- and monoiodoanilides of salicylic acid, for example, the o-chloroanilide, m-chloroanilide, p-chloroanilide or p-bromoanilide. Among the polyhalogenated compounds, it is necessary to mention especially the dichloroanilides, for example, 3, 4-dichloroanilide, 2, 4-dichloroanilide or 3, 5-dichloroanilide. It is also possible to involve derivatives containing different halogen atoms, for example, the chlorobromoanilides. The anilides can also have other substituents in the nucleus of the aniline, in particular lower alkyl or alkoxy groups. Such derivatives can come from toluidines or methoxyanilines. For example, p-chloro-o-toluidide or o-methoxy-m-chloroanilide will be mentioned. These compounds are known or can be prepared according to known methods. The reaction of salicylic acid with a halogenated aniline, with addition of phosphorus trichloride, in the presence of a solvent such as toluene, is suitable, for example, for the preparation of such anilides.

Instead of the free anilides, their water-soluble salts, for example, the sodium salt, potassium salt or salt of certain amines, can also be used with advantage in the present process. The treatment of the materials to be protected takes place advantageously with aqueous solutions of the salts which were mentioned. It is possible nevertheless also to use free anilides, dissolved in organic solvents or in aqueous suspension. In practice, one operates according to the usual processes of impregnation, for example, by dipping, padding or spraying. Other fungicides, insecticides and/or bactericides can also be added to the solutions or suspensions of the fungicides according to the invention, for example, when the material to be treated must also be protected at the same time from the attack of insects, bacteria or molds which are resistant to the fungicides according to the invention. The addition of bactericides is unnecessary in many cases, since it has been observed that, for example, salicylmonochloroanilide, contrary to salicylanilide, has a considerable bacteriostatic or bactericidal activity. This property of a group of the new fungicides according to the invention thus makes possible, for example, the protection of textiles from rotting in the earth.

When the material is treated with halogenated derivatives of salicylanilide, which are substituted in the aniline nucleus by one or more halogen atoms and in which the total quantity of halogen introduced per gram molecule amounts to more than 36 g, and which can also be substituted, moreover, optionally, in the aniline nucleus by lower alkyl or alkoxy groups, the treated material benefits from a protection which persists even after immersion in running water for several hours. This effect is not obtained when the ordinary salicylanilide is used, since the protection created by this compound disappears when the treated material is immersed in water. For example, the dichloroanilides and the p-bromoanilide mentioned at the beginning fulfill the conditions defined above.

The quantities of fungicides which must be applied to the materials vary according to the conditions of use of the material and the intensity with which the protected material is exposed to the attack of the lower fungi. Usually, quantities of a few 1/10 per thousand to a few per cent are sufficient for providing complete protection.

Among the lower fungi from whose attack the cellulose-containing material can be protected, the following will be mentioned, for example: *Chaetomium globosum*, *Synosporium biguttatum*, *Memnoniella echinata* and *Stachybotris atra*.

The worked materials which can be treated according to the invention can have the most diverse compositions, as far as they are subjected only to attack by lower fungi. Considered above all are materials containing cellulose, and in particular, textile materials which can be finished or not finished. We will mention threads, spun yarns or fabrics made of natural fibers containing cellulose, such as cotton, flax, hemp, jute, and moreover, the fabrics of regenerated cellulose. Furthermore, it is also possible to treat and protect paper and wood as well as objects containing such materials, and moreover, fibrous materials not containing cellulose as far as they are exposed to attack by lower fungi.

In the following nonlimiting examples and except when indicated otherwise, parts are understood to be by weight. Moreover, the ratio of parts by weight to parts by volume is the same as that which exists between the kilogram and the liter; the temperatures are indicated in degrees centigrade.

Example 1

Cotton was impregnated by a padding machine with solutions of various concentrations of sodium salts of salicylanilide and of salicyl-m-chloroanilide in such a way that 100% liquid absorption occurred, counted based on the fabric weight, and then it was dried. Strips of cloth were then seeded with the lower fungus *Chaetomium globosum* and incubated for 15 days at 30°C on agar gel containing appropriate inorganic salts. The intensity of growth of the lower fungus on the various strips was then determined, and the reduction of the breaking strength of the fabric was measured. In the following table, the average values of 10 tests have been given.

Indicated in column I is the concentration of the sodium salt in the impregnation bath; given that the quantity of liquid absorbed by the cotton is 100%, the numbers also correspond to the concentration in the fabric. Indicated in column II is the intensity of growth of the lower fungus; the meaning of symbols used is the following:

++++ Very intense growth;

+++ Intense growth;

++ Slight growth;

+ Barely perceptible growth;

-No growth.

Indicated in column III is the reduction in percent of the breaking strength.

The symbols used mean:

a = reduction by 90 to 100%, that is to say that the fabric no longer has any breaking strength;

b = reduction by 30 to 70%, on average 50%;

c = reduction by 0 to 10%, that is to say that the fabric practically kept its breaking strength.

ANILIDE DE L'ACIDE SALICYLIQUE (1)		
I	II	III
Sans addition (3)	++++	a
0,125 %	++++	a
0,25 %	+++	b
0,5 %	—	c
1,0 %	—	c

M-CHLORO-ANILIDE DE L'ACIDE SALICYLIQUE (2)		
I	II	III
Sans addition (3)	++++	a
0,125 %	+++	b
0,25 %	—	c
0,5 %	—	c
1,0 %	—	c

Key: 1 Salicylanilide
2 Salicyl-m-chloroanilide
3 Without addition*

It emerges from the table that salicyl-m-chloroanilide is approximately twice as active as salicylanilide.

The salicyl-m-chloroanilide used in this example can be prepared as follows:

To a mixture of 34.5 parts of salicylic acid and 32 parts of m-chloroaniline in 250 parts of anhydrous toluene, 14 parts of phosphorus trichloride are added dropwise over approximately 15 min at 50-60°C with stirring. The reaction mixture is then heated to boiling for 3-4 h, with a return condenser, which separates gaseous hydrochloric acid and produces a clear solution. When, after a certain time, hydrochloric acid is no longer given off, the reaction is finished. The reaction solution is allowed to cool to approximately 80°C, and 250 parts of water and approximately 100 parts of a 10% sodium carbonate solution are added with stirring, so that finally, the reaction mixture has only a slight acid reaction to paper containing bright yellow. The mixture obtained then undergoes steam distillation, which causes the toluene to be recovered and a small amount of unreacted chloroaniline to be eliminated. From the steam distillation residue,

* [Editor's note: In the tables, commas in numbers represent decimal points.]

the anilide precipitated in crystalline form is filtered and washed with water. The salicyl-m-chloroanilide, dried under vacuum at approximately 100°C, is a colorless powder which can be recrystallized from benzene or alcohol and which melts at 167-168°C (not corrected).

In order to prepare the sodium salt, which is soluble in water, 11 parts of aniline are dissolved hot in 100 parts of water and 5 parts by volume of a concentrated sodium hydroxide solution; then, the solution is evaporated to dryness. A colorless powder is thus obtained, which dissolves in water giving a clear solution.

Salicyl-o-chloroanilide and salicyl-p-chloroanilide can also be prepared by the same method.

Melting point of salicyl-o-chloroanilide = 164.5 to 165°C (not corrected).

Melting point of salicyl-p-chloroanilide = 168 to 169°C (not corrected).

Example 2

Strips of a cotton fabric were impregnated as described in Example 1. The fabric strips were buried in compost having a water content of 30% and left for 15 days at 30°C in the compost. They were then removed, and the growth of lower fungi and bacteria was determined, as was the reduction of the breaking strength of the fabric. Indicated in the following table are the average values of ten tests; the symbols are the same as in Example 1.

ANILIDE DE L'ACIDE SALICYLIQUE (1)			M-CHLORO-ANILIDE DE L'ACIDE SALICYLIQUE (2)		
I	II	III	I	II	III
Sans addition (3)	++++	a	Sans addition (3)	++++	a
0,25 ‰	++++	a	0,25 ‰	+++	b
0,5 ‰	++++	a	0,5 ‰	--	c
1,0 ‰	++++	a	1,0 ‰	—	c
2,0 ‰	++++	a	2,0 ‰	—	c

Key: 1 Salicylanilide
2 Salicyl-m-chloroanilide
3 Without addition

It emerges from the table that salicylanilide does not protect cotton fabric from rotting in the earth, whereas the addition of 0.5% or more of salicyl-m-chloroanilide, with respect to the weight of the fabric, is capable of protecting it from attack by microorganisms present in the earth.

Example 3

One proceeds as in Example 1 or in Example 2 but using salicyl-p-chloroanilide instead of salicyl-m-chloroanilide; one arrives at similar results.

Example 4

Spun cotton yarn is sprayed during its winding on a spool with a solution of salicyl-m-chloroanilide sodium salt. The yarn is thus protected from attack by lower fungi.

Example 5

A cotton fabric was impregnated by a padding machine with solutions of various concentrations of the sodium salts of salicylanilide, of salicyl-2, 4-dichloroanilide, and of salicyl-3, 4-dichloroanilide, in such a way that 100% liquid absorption occurred, counted based on the fabric weight. Half of the strips of fabric then underwent immersion for 24 h in running water. After that, all strips of fabric were seeded with the lower fungus *Chaetomium globosum* and incubated on agar gel containing appropriate inorganic salts for 15 days at 30°C. The intensity of growth of lower fungus on the various strips was then determined, and the reduction of the breaking strength of the fabric was measured. In the following table, the average values of ten tests are summarized.

Indicated in column I is the concentration of the sodium salt in the impregnation bath; given that the quantity of liquid absorbed by the cotton is 100%, the numbers correspond to the concentration in the fabric. Indicated in column II is the intensity of growth of lower fungus, and indicated in column III is the reduction in percent of the breaking strength; the symbols are the same as in Example 1.

COMPOSÉ (1)	TISSU NON LAVÉ À L'EAU (6)			TISSU LAVÉ À L'EAU (7)		
	I	II	III	I	II	III
Sans addition (2)	% —	++++	a	% —	++++	a
Anilide de l'acide salicylique (3)	0,125	++++	a	0,125	++++	a
	0,25	++,+++	b	0,25	++++	a
	0,5	—	c	0,5	++++	a
	1,0	—	c	1,0	++++	a
	2,0	—	c	2,0	++++	a
3,4-dichloro-anilide de l'acide salicylique (4)	0,125	++,+++	b	0,125	++++	a
	0,25	—	c	0,25	++	b
	0,5	—	c	0,5	—	c
	1,0	—	c	1,0	—	c
	2,0	—	c	2,0	—	c
2,4-dichloro-anilide de l'acide salicylique (5)	0,125	++	b	0,125	++++	a
	0,25	—	c	0,25	++++	a
	0,5	—	c	0,5	—	c
	1,0	—	c	1,0	—	c
	2,0	—	c	2,0	—	c

Key: 1 Compound
2 Without addition
3 Salicylanilide
4 Salicyl-3, 4-dichloroanilide
5 Salicyl-2, 4-dichloroanilide
6 Fabric not washed with water
7 Fabric washed with water

It emerges from the table that salicylanilide is completely eliminated by the water during immersion, since even using high concentrations which protect the nonimmersed fabric, there is no protection in the case of the immersed fabric. Contrary to this, the dichloroanilides also protect the immersed fabric at concentrations of 0.5% and more. In the case of lower concentrations, a slight decrease of activity occurs because of the immersion. It also emerges from the table that the dichloroanilides are approximately twice as active as the ordinary anilide,

since in the case of the nonimmersed fabrics, addition of 0.25% of dichloroanilide is sufficient for complete protection, which can only be attained with 0.5% of the ordinary anilide.

The 3, salicyl- 4-dichloroanilide used in this example can be prepared as follows:

14 parts of phosphorus trichloride are made to run at 50-60°C over 10-15 min into a mixture of 34.5 parts of salicylic acid and 40.5 parts of 3, 4-dichloroaniline in 250 parts of toluene. The reaction mixture is then heated to boiling for 4 h, with a return condenser, which separates gaseous hydrochloric acid and produces an almost clear solution. When absolutely no more hydrochloric acid is given off, the reaction is finished, and the reaction solution is allowed to cool to approximately 80°C; 250 parts of water and approximately 100 parts of 10% sodium carbonate solution are added with stirring, so that finally, the reaction mixture has a slightly acid reaction to paper containing bright yellow. It then undergoes steam distillation in order to completely eliminate toluene and unreacted dichloroaniline. The anilide precipitated in crystalline form from the distillation residue is separated by filtration and then washed with water. The salicyl-3, 4-dichloroanilide, dried at approximately 100°C under vacuum, is a colorless powder. The melting point of the anilide recrystallized from alcohol is 211.5-212.5°C (not corrected).

In order to prepare the sodium salt, which is soluble in water, 10 parts of the anilide are dissolved hot in 120 parts of water and 5 parts by volume of a concentrated sodium hydroxide solution; then, the solution is evaporated to dryness. A colorless powder is thus obtained, which is soluble in water giving a clear solution.

Salicyl-2, 4-dichloroanilide and salicyl-3, 5-dichloroanilide can also be accessed in the same manner, starting from the corresponding dichloroanilines.

Melting point of salicyl-3, 5-dichloroanilide = 211.5-212.5°C (not corrected).

Melting point of salicyl-2, 4-dichloroanilide = 189-189.5°C (not corrected).

Example 6

One proceeds as described in Example 5 but using salicyl-3, 5-dichloroanilide, instead of the dichloroanilide which is used there, and similar results are obtained.

Summary

[Claims]

The invention relates particularly to the following points:

1. A process for the protection of worked materials from the attack of the lower fungi which are capable of attacking them, characterized by the fact that said materials are treated by salicylanilides that are halogenated in the aniline nucleus;

a. The treatment is carried out with aqueous solutions of salts of the derivatives defined under a;

b. Monohalogenated derivatives which can also be substituted optionally, in the aniline nucleus, by lower alkyl or alkoxy groups are used;

c. Salicyl-m-chloroanilide sodium salt is used;

d. Salicyl-p-chloroanilide sodium salt is used;

e. Halogenated derivatives of salicylanilide which are also substituted in the aniline nucleus by one or more halogen atoms are used, in which the total quantity of halogen introduced per gram molecule amounts to more than 36 g, and which can also be optionally substituted in the aniline nucleus by lower alkyl or alkoxy groups;

f. Monobrominated derivatives are used;

g. The salicyl-p-bromoanilide sodium salt is used;

h. Polyhalogenated derivatives are used;

i. Dihalogenated derivatives are used;

j. Dichlorinated derivatives are used;

k. Salicyl-3, 4-dichloroanilide sodium salt is used;

l. Salicyl-2, 4-dichloroanilide sodium salt is used;

m. Salicyl-3, 5-dichloroanilide sodium salt is used;

n. Insecticides, bactericides and/or other fungicides are moreover used;

o. Worked cellulose-containing materials are treated;

p. Textile materials are treated;

q. Cotton fabrics are treated;

r. Worked cellulose-containing materials are protected from attack by the lower fungi which degrade cellulose;

s. Cellulose-containing textile materials are protected from attack by the lower fungi which degrade cellulose;

t. Cotton fabrics are protected from attack by said lower fungi.

2. As new industrial products, the materials treated by the process above.

3. As new industrial products, salicylanilides, which are halogenated in the aniline nucleus.

Company known as: CIBA (Joint-Stock Company)
By proxy:
H. Gouvernal